# Capacity Fade Studies on Spinel Based Li-Ion Cells

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#### Introduction

The objective of this paper was to study the performance of Lithium-ion batteries with spinel based cathodes. First, we want to optimize the discharge capacity of the cell based on the charge current, end potential and total charging time. Next, we compare the capacity fade of cells charged at different rates to a common end potential and discharged at the same current. The goal here is to minimize the capacity loss with cycling by choosing an optimum charging current. Finally, we study the causes for the capacity fade in spinel based Li-ion batteries.

# **Results and Discussion:**

All studies were done on Cellbatt® Li-ion cells with an initial capacity of 1050 mAh. The charging protocol involved applying constant current (CC) and constant voltage (CV) at different times during cell charging. Instead of holding the charging time constant, we monitor the decay in current with time during the constant voltage part. When the current reaches 50 mA, we stop charging. In order to establish the optimum cut-off voltage, cells were charged at a constant current of 1 A to different end voltages. The potential was held constant till the current decayed to 50 mA. Subsequently the cells were discharged at a constant current of 1 A. Figure 1 shows the discharge profiles for Cellbatt® cells charged to various cut-off potentials. Since, no difference in capacity is seen between charging at 4.17 V and 4.3 V, in subsequent studies the cell was charged to 4.17 V. This was done primarily to prevent oxidation of the electrolyte and the spinel. According to Aurbach et al.1, cycling spinel in the potential range 3.5-4.2 V caused no Mn dissolution. Batteries after different charge-discharge cycles were analyzed using impedance spectroscopy and linear polarization. Some batteries were cut-open and both positive and negative electrodes were analyzed using XRD, SEM and EDAX. Solartron SI 1255 HF Frequency Response Analyzer and Potentiostat/Galvanostat Model 273A were used for the electrochemical characterization studies. Charge-discharge studies were carried out in the potential range of 3.0-4.17 V. The cells were left on open circuit for 1hour and after the potential stabilized, impedance studies were performed. The cell was stable during the experiments and its voltage changed less than 1 mV. EIS measurements were done on the cells at both charged and discharged states. The impedance data generally covered a frequency range of 0.001 to 10000Hz. A sinusoidal AC voltage signal varying by  $\pm 5 \text{mV}$ was applied.

This paper focuses on studying the performance of Li-ion cells using LiMn $_2$ O $_4$  as the positive electrode material. The capacity of the cell has been optimized based on varying the charging current and the end potential. The capacity fade of these batteries has been studied at different charge currents, namely 0.1 A, 0.25 A, 0. 5 A, 0.75 A and 1 A. The discharge rate for all cells was kept constant at 1 A. The lowest capacity fade is seen for the cell charged at 0.5 A indicating that this was optimum charging current for these batteries. For all

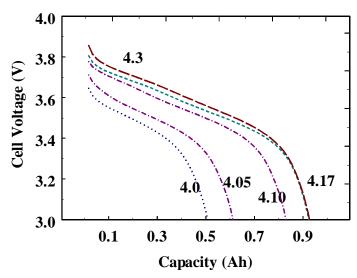
charge currents, the resistance of the  $LiMn_2O_4$  cathode remains lower than that of the carbon anode with cycling. XRD studies of carbon and  $LiMn_2O_4$  at different cycles, reveals no structural changes. However, the lattice constants vary with cycling indicating changes in the lithium intercalated at both electrodes<sup>2</sup>. Further studies are being done to understand the cause for the capacity fade.

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## References

- 1. D. Aurbach et al., J. Power Sources, **81-82**, 472 (1999).
- 2. Haitao Huang, Colin A. Vincent and Peter G. Bruce, J.Electrochem. Soc., **146**, 3649 (1999).



**Figure 1.** Change in discharge capacity for Li-ion cells charged to different potentials